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UNITED STATES ATOMIC ENERGY COMMISSION

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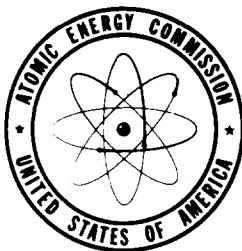
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September 15, 1948

Battelle Memorial Institute
Columbus, Ohio



Technical Information Extension, Oak Ridge, Tennessee

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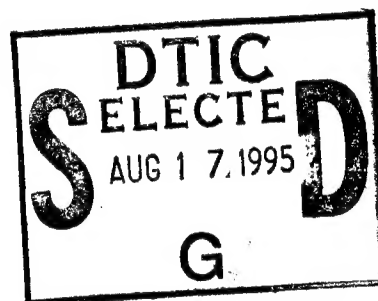
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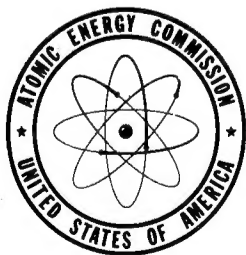
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RECOVERY OF URANIUM FROM SHALES

(A. E. Bearse, Supervisor)

INTRODUCTION

The objective of this project is to develop a practical process for recovering uranium from domestic low-grade shales. Recent samples of these shales from Tennessee have been found to contain from 0.005 to 0.009 per cent of uranium. Preceding topical reports on this project (BMI-JDS-101 and -130) have described the work carried out prior to June 30, 1948. The present report is concerned with research since that date and up to September 15, 1948.

In the topical report of June 30, 1948, it was shown that by roasting shale under controlled conditions on a small scale approximately 70 per cent of the uranium could be solubilized and extracted into a sodium carbonate solution. It was indicated that dilute sulphuric acid might be used advantageously instead of sodium carbonate. Recent work has been directed in part toward increasing the scale of operations in the roasting step. Several types of roasting equipment are being investigated.

Leaching studies have been directed more and more toward the use of dilute sulphuric acid, since this acid could be produced readily from the oxides of sulphur obtained in large amounts on roasting the shale. Attention has been given to building up the uranium content of leach solutions by countercurrent operation.

Although the work on recovery of fuel values from shale has been integrated with the work on uranium recovery, the fuel studies will be covered separately in a future topical report.

SUMMARY

Recent work has shown that uranium extractions in the 70-per cent range can be obtained by suitable leaching of roasted shale with dilute sulphuric acid. The leaching can be carried out at room temperature in a short period of time with agitation. Percolation leaching does not appear to be feasible for this type of material. Advantages of a sulphuric acid leach over the previously used sodium carbonate leach are that the shale contains sufficient sulphur to provide the acid for the leaching operation and that recovery of uranium from the leach liquor should be simpler.

The importance of roasting conditions on subsequent extraction of uranium has been demonstrated in attempting to carry out the roasting operations on a larger scale. Although the 70-per cent uranium extraction has been realized on shale roasted in a 20-pound batch, roasting times have been excessive. Fluidization retorting of shale with steam has been shown to give a product which can be roasted in a tube and leached successfully. However, fluidization roasting to date has not given satisfactory material for the uranium extraction step. It is believed that future work on fluidization roasting, possibly with recycle of a portion of the off-gases, will give a more suitable material for leaching.

Roasting studies in a muffle furnace and in a horizontal rotating tube furnace have further demonstrated the importance of obtaining a

complete roast if satisfactory uranium extraction is to be secured.

Studies on uranyl sulphate indicate that thermal decomposition of this material is significant at 1300-1400°F. (700-750°C.) and may be an important factor in the decreased uranium extractions obtained on shale after roasting at high temperatures.

Although many different reagents have been investigated for the leaching of uranium from shale, only solutions of sodium carbonate, sulphuric acid, and possibly sulphurous acid are being considered seriously at the present time. Use of the "off-gases" from the roasting operation to prepare an aqueous solution for the leaching step has shown promise. The leach solution in this case was found to be relatively low in iron and aluminum.

Enrichment of uranium in a dilute sulphuric acid leach solution has been accomplished by leaching successive batches of roasted shale with the same solution. A level of 150 milligrams of uranium per liter has been obtained, and it is believed that removal of uranium from a solution of this concentration should be feasible. Further information is being secured on the build-up of iron, aluminum, and other ions in operations of this type.

A series of runs on a variety of shale samples indicates that the over-all process of roasting followed by leaching with aqueous sodium carbonate (and presumably with dilute sulphuric acid) can be applied generally. Only moderate variations in uranium extraction were observed on shales differing considerably in uranium and sulphur content.

Several shale samples have been received recently from the U. S. Geological Survey which contained 0.009 per cent of uranium. In general, there seems to be a rough correlation between the amounts of uranium and sulphur found in different samples. It is interesting that an iron pyrite fragment taken from one sample of shale contained nearly twice the uranium content of the sample as a whole, indicating possible association of the uranium with the pyrite. However, other selected portions of the same sample, which were higher in pyrite than the sample as a whole, contained slightly less uranium. Additional work now in progress should clarify this subject.

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

Description of Shale Samples

The general chemical composition of some of the shale samples under investigation was presented in the preceding topical report, (EMI-JDS-130, June 30, 1948). Currently, only sulphur, uranium, and loss on ignition are being determined; these data on the more recent samples are recorded in Table 1.

It has been noted that all of the shales contain appreciable quantities of sulphur, ranging from 1.5 to 8.6 per cent. Analysis of a fairly typical shale (No. 1207-100) indicated that most of the sulphur (nearly 85 per cent in this case) occurred in the form of iron pyrite. In many of the higher grade shales, pyrite is visible, in thin bands, in individual specimens.

TABLE 1. SHALE SAMPLES AND ANALYSES

U. S. G. S. No.	B. M. I. No.	Composition, Per Cent		
		U	S	L.O.I.
LC-11-102B	1207-106	0.0045	3.2	15.9
LC-15B	1207-107 ⁽¹⁾	0.0080	6.9	21.8
LC-33-101B	1207-108	0.0087	7.3	23.9
R-C2-113	1207-109	0.0092	8.6	23.3
R-S16-117B	1207-110 ⁽²⁾	0.0089	1.56	14.3

(1) Shipment of shale from Carbide Y-12; reputedly duplicate of LC-15C (1207-100).

(2) Very badly weathered shale; unlike any other sample in appearance.

There is quite evidently some relationship between the sulphur content and the uranium content of the shales investigated; tabulation of the shales in order of ascending uranium content (Table 2) shows this quite clearly. It is felt that more precise determinations of the uranium would result in local shifting of relative positions, further smoothing the data. In some of the shale samples, it is probable that weathering has reduced the sulphur content.

Analysis of a fragment of shale No. 1207-108 which was principally pyrite showed a uranium content of 0.016 per cent, whereas the average for this shale was only 0.0087 per cent, indicating in this case a definite enrichment in the pyritic fraction.

However, in another case a pyrite seam taken from a lump of the same sample of shale showed only 0.0070 per cent of uranium which was lower than the average for the sample. Further work is in progress to determine whether or not there is an association of the uranium with the pyrite.

Roasting and Retorting Studies

Roasting studies on shale have been concerned with the use of different atmospheres to increase conversion of uranium into a form which could be removed by subsequent leaching. Efforts have also been directed toward investigating methods of roasting shale on a larger scale in anticipation of future test plant studies.

TABLE 2. SHALES IN ORDER OF ASCENDING URANIUM CONTENT

U. S. G. S. No.	B. M. I. No.	Composition, Per Cent	
		U	S
LC-11-102B	1207-106	0.0045	3.2
LC-11 B-1	1207-103A	0.0055	3.7
S-100-46	1090-4	0.006	5.9
LC-11 B-2	1207-103B	0.0065	4.4
LC-6 B-2	1207-101B	0.0065	5.1
LC-6 B-1	1207-101A	0.0070	5.4
BR-154-46	1090-1	0.0070	6.8
LC-6 B-3	1207-101C	0.0075	4.7
LC-17B	1207-104	0.0075	5.0
LC-15C	1207-100	0.0075	6.9
LC-15B	1207-107	0.0080	6.9
LC-10B	1207-102	0.0080	5.1
R-S1-B	1207-105	0.0080	7.0
LC-33-101B	1207-108	0.0087	7.3
R-S16-117B	1207-110	0.0089	1.5 ⁽¹⁾
R-C2-113	1207-109	0.0092	8.6

(1) Unusual shale, apparently very badly weathered and oxidized.

Larger Scale Roasting in a Horizontal Tube Furnace

Several batches of shale have been roasted in larger capacity equipment than the laboratory apparatus used to date in the experimental program. The equipment used was a 10" by 24" horizontal drum enclosed in an air chamber which was heated electrically. The drum was supported by hollow shafts and provisions were made for rotation of the drum and for introduction of air into the drum. This equipment provided about a 45-fold increase in capacity over that obtained in the laboratory apparatus. Batches of 5,000 to 9,000 grams (11 to 20 pounds) were used.

Runs were made on four shales, as shown in Table 3. The particle size of the large-scale batches covered a wide range, from about 5 per cent minus 10 mesh to a relatively finely ground shale having 90 per cent minus 30 mesh and 60 per cent minus 100 mesh.

Leaching was carried out under varied conditions with different lixiviants as indicated in the table. A uranium extraction of 70 per cent was obtained with sodium carbonate or sulphuric acid in two of the eight runs. In these cases, the material was roasted for 60 hours or longer. Shorter roasting times, even at higher temperatures, gave lower extractions. Apparently the lower results were due to incomplete penetration of air into the shale particles.

Results indicate that the smaller particles, during the early stage of partial roasting, were roasted better than the larger particles - as measured by percentage extraction. This is to be expected if the reaction

TABLE 3. LARGE-SCALE ROASTING EXPERIMENTS

Roasting Equipment: 10" by 24" horizontal steel drum heated externally by electricity

Shale No.	Particle Size	Wt. of Charge, Kg.	Roasting Temp., °F.	Roasting Time, Hours	Rotation of Drum, R.P.M.	Air Flow, l. per Minute	Wt. Loss on Roasting, Per Cent	Leaching Conditions	Uranium Extrac-tion, Per Cent
1090-9	55% $\frac{1}{2}$ " to +8 mesh 8% -50 mesh	6	930	6	1/4	10	20	2% H ₂ SO ₄ followed by 15% Na ₂ CO ₃ , both at 180°F.	37
1207-105	50% $\frac{1}{2}$ " to +8 mesh 5% -50 mesh	9	750 930 1020	19 8 $\frac{80}{107}$		0 12 12	-	2% H ₂ SO ₄ at room temperature	70
1207-107	80% +30 mesh 8% -100 mesh	5	930	30	1/4	5	22.2	15% Na ₂ CO ₃ at 180°F.	10
1207-107	Same as above	5	1020	60	0	9	18.6	15% Na ₂ CO ₃ at 180°F. 2% H ₂ SO ₄ at room temp.	70 73
1207-107	Same as above	5	1110	40	0	9	20.7	15% Na ₂ CO ₃ at 180°F. 2% H ₂ SO ₄ at room temp.	50 58
1207-107	10% +30 mesh 60% -100 mesh	5	1110	40	0	9	21.8	2% H ₂ SO ₄ at room temp. 2% H ₂ SO ₄ at 180°F.	50 62
1207-108	92% +10 mesh	6.8	1110	6	1/4	11	18.2	Aqueous SO ₂ at 180°F.	7
1207-108	Same as above	6.8	1110	4	1/4	15 to 50	18.3	Water at 180°F.	< 10

rate depends on the rate of gaseous diffusion to the interior of the particle. However, some other change apparently took place, which improved the percentage extraction, some time after the appearance of a uniform red iron oxide coloration. When completely roasted, the large particle gave the same uranium extraction as the small particles (see Table 4).

Loss in weight during the roasting process was no indication of the percentage extraction obtained on the product, as indicated by these test runs.

The data indicate that it was immaterial, under the conditions of these tests, whether or not there was movement of the shale during roasting.

Preheating the air supplied to the hot shale appeared to give improved penetration into the larger particles in a given period of time.

Roasting in a Vertical Tube Furnace

Other large scale roasting experiments have been carried out in a vertical tube furnace. The roasting chamber consisted of a 2-foot length of iron pipe, 4 inches in diameter. The shale was supported in the pipe by a base plate perforated with 1/16-inch holes. A preheater was provided for the air introduced. One object in using this type of furnace was to obtain more intimate contact of air with the shale than was possible in the horizontal furnace already described.

TABLE 4. CHANGE IN EXTRACTABILITY WITH ROASTING TIME

(See Table 3, Test 2, for roasting conditions.)

Total Roasting Time, Hours	<u>Particle Size Distribution</u>		Uranium Extracted, Per Cent
	Mesh Size	Per Cent	
8	+8	50	21
	-8 +30	37	22
	-30	13	41
16	+8	49	30
	-8 +30	38	32
	-30 +50	8	31
	-50	5	39
88	+8	63	72
	-8 +30	28	69
	-30 +50	5	69
	-50	4	70

(1) Extraction by leaching with 2 per cent sulphuric acid at room temperature for one hour.

Note: +30 mesh material ball milled before extraction.

Three roasts were performed in the vertical tube furnace using 3.0 kg. of shale in sizes ranging from +16 mesh to -2 inch. Preheated air was used as the source of heat in all. In these roasts, gases were discharged from the furnace at atmospheric pressure; Table 5 summarizes the pertinent data.

The temperatures of these roasts were not constant as indicated in Table 5. Variation in the temperature of the entering air was caused by cutting the preheater off and on during the roasts. The bed temperature was difficult to control after it reached 800°F. (425°C.) but could be kept at, or above, 800°F. without the preheater.

Sintering of the shale bed occurred in all roasts except the one in which -2" +1/2" shale was treated. The fact that no sintering occurred in this case may be due to one, or both, of two factors: the size of the shale or the bed temperature. The maximum temperature reached in this roast was 1265°F. (685°C.), which was lower than in any of the others. Other experiments have indicated that the minimum sintering temperature of shale is about 1800°F. (980°C.). This is not borne out by the fact that some sintering occurred in the roast which was carried to a maximum recorded temperature of 1430°F. Possibly local temperatures exceeded the recorded temperature.

Not all of the carbonaceous matter was expelled from the shale in any of these roasts as the weight loss and appearance of the ore indicated. In all cases, the material on the outer surfaces of the pieces of shale was carbon free, but the cores contained carbonaceous

TABLE 5. ROASTING STUDIES IN A VERTICAL TUBE FURNACE

Shale Sample	Size	Wt. Loss, Per Cent	Bed Height, Inches	Time, Hours	Approx. Air Flow, l./Min.	Press., P.S.I.G.	Sintering Occurred	Temperature of Air In Bed	Temperature of Air Out	Uranium Extracted, % (1)
1207-105	- $\frac{1}{2}$ " +8M.	16.9	12	4.7	20	0	Yes	About 815 800. to 2290.	About 800.	38 (2) (9)
1090-4	-2" + $\frac{1}{2}$ "	18.7	20	14	20	0	No	About Max. 800. 1265.	-	36
1207-105	+16M.	20.1	14	6.7	20	0	Yes	About Max. 800. >1500.	About 500.	24 (2) (27)

(1) Extraction by leaching with 1.8 per cent sulphuric acid at room temperature for two hours.

(2) Figures in parentheses indicate extraction on fused portion.

matter. Generally, the sintered material seemed to be richer in carbonaceous matter than the unsintered portions.

Recovery of uranium from these roasted shales by leaching with 1.8 per cent sulphuric acid gave a maximum of about 50 per cent.

Further work with the vertical tube furnace will include roasting finer shales and determining the minimum temperature at which sintering occurs.

Roasting in a Muffle Furnace

The importance of completeness of roasting, when sodium carbonate is the lixiviant, was demonstrated in a series of tests in which No. 1207-100 shale was roasted, without rabbling, in a muffle furnace. The top portion, which was salmon-colored and was considered to be fully roasted, was separated from the dark, bottom portion, and the two portions were leached separately in 15 per cent sodium carbonate solutions. Whereas, extractions in the 70-75 per cent range were obtained on the completely roasted portion, only 15-20 per cent extractions were obtained on the partially roasted material.

Previous work has shown that complete roasting of the shale in a muffle furnace can be accomplished with a small amount of rabbling.

Fluidization Retorting and Roasting

In view of the possibility of operating on a large scale under controlled conditions, fluidization retorting and roasting of shale

are being investigated. Uranium recovery studies are being run in conjunction with the experimental work on recovery of fuel values by fluidization techniques.

Experiments have been carried out in a $3\frac{1}{2}$ -inch I.D. Pyrex glass column with a 60° cone at the bottom in which was placed a 5/8-inch steel ball. This column was operated batchwise, the charge being one pound of shale No. 1090-4 which had been crushed to pass a 10-mesh screen with 86 per cent being retained on a 100-mesh screen.

The bed of ore was made fluid and the retorting operation carried out by means of superheated steam. A run was made wherein the shale was first retorted at 800°F (425°C.) for 30 minutes giving an 8.7 per cent weight loss. Air was then passed through and the ore was roasted in a fluidized condition at 1585°F. (860°C.). This last operation also required about 30 minutes and gave an over-all weight loss of 31.3 per cent comparison, a fifty-gram sample of the raw shale and a like sample of the retorted material, taken just before the air roasting operation, were roasted in horizontal tubes. These two samples, as well as a sample of the fluidized roast, were given similar leaches.

The results (Table 6) indicate the fluidization retorting with steam was not detrimental to subsequent roasting and leaching operations. However, fluidization roasting at 1585°F. (860°C.) decreased uranium recovery markedly.

TABLE 6. EFFECT OF FLUIDIZATION RETORTING
AND ROASTING ON URANIUM EXTRACTION

Starting Material: Shale No. 1090-4

	Raw Shale	Shale Retorted 30 Minutes With Steam at 800°F.	Shale Retorted and then Roasted by Fluidization at 1585°F.
Roasting Temp. - °F.	1112 ⁽¹⁾	1112 ⁽¹⁾	1585 ⁽²⁾
Roasting Time - Hours	3	3	0.5
Wt. Before Roast (Grams)	50.0	50.0	-
Wt. After Roast (Grams)	42.5	43.7	-
Per Cent Uranium Recovered in Leach ⁽³⁾	58	64	23

(1) Refers to roasting temperature on 50-gram sample in a horizontal tube.

(2) Refers to roasting temperature in fluidization unit.

(3) Leach was by agitation for one hour at room temperature with 200 cc.
of 2 per cent sulphuric acid on equivalent of 50 grams of raw shale.

In another series of experiments several samples of Shale No. 1090-2 which had been retorted at 840°F. (450°C.) for 14 hours in an externally heated rotary furnace were roasted batchwise by fluidizing with air and with oxygen. A two-inch I.D. Pyrex glass tube was used. The shale was brought to approximately 700°F. (370°C.) by external heat before fluidizing. The roasted product gave rather low uranium recoveries when subsequently leached with sulphuric acid solution (Table 7).

A possible explanation of the poor extractions is that in the fluidization apparatus used, no provision was made for recycling the off gases. As a result, the oxides of sulphur produced during the roasting were removed rapidly from the fluidized shale. By gas recycling, it should be possible to build up the concentration of oxides of sulphur to a point where sulphating conditions would prevail. This should permit higher uranium recoveries.

Effect of Retorting on Removal of Sulphur from Shale

Since it is conceivable that the processing of shale might involve a retorting step followed by roasting, it was desired to learn the amount of sulphur retained in the shale after retorting. The sulphur content after retorting is significant if a sulphating atmosphere is required for the roasting operation.

TABLE 7. RESULTS OF LEACHING SHALE WHICH HAD BEEN ROASTED BY FLUIDIZING SUBSEQUENT TO RETORTING

Shale: G-1090-2 retorted at 840°F. for 14 hours and roasted as indicated.

Leach: By agitation at room temperature for two hours with 200 cc. of 5 per cent sulphuric acid per 100 grams of ore.

Sample	Weight, Grams	Mesh, Size	Atmosphere	Temperature, °F.	Approximate Time, Minutes	Weight Loss (1), Per Cent	Uranium Recovery, Per Cent
3288-751	150	20-40	Air	1100-1200	15	24.8	38
3288-752	450	20-40	Air	900-1000	45	24.8	28
3288-761	200	10-70	Air	1080	25	24.0	39
3288-762(2)	200	70-140	Air	1100-1300	20	20.7	33
3288-781(2)	300	20-40	Oxygen	1100-1300	25	23.6	30

(1) Based on raw shale.

(2) Raw shale.

Samples of Shale No. 1090-2, each weighing 26 pounds, were retorted in an externally heated horizontal rotary furnace. In one case, the temperature was maintained at 840°F. (450°C.) for 14 hours and in the other at 800°F. (425°C.) for 24 hours. In each case, a determination of the sulphur content, both pyritic and total, was made before and after retorting. It was found that about one-half of the pyrite present was decomposed to ferrous sulphide (FeS) in this retorting operation, thus about 25 per cent of the oxidizable sulphur in the raw shale was lost, see Table 8. It is possible that this loss of sulphur might be lowered if the retorting operation were carried out in a fluid bed where a much shorter residence time would be necessary.

The oxidizable sulphur content after retorting was of interest since it is this sulphur which would be necessary to produce a sulphating roast. If oxygen-enriched air were used in roasting, the stock gases might also be used as a source of sulphuric acid for leaching purposes.

Chlorination Roasting

A series of chlorination roasts on several different screen-size fractions of Shale No. 1207-100 indicated that extraction increased with decreasing particle size (Table 9). The finest (-325 M) fraction was an exception to this, but the data can possibly be reconciled by presuming that appreciable volatilization occurred. The reaction with chlorine was considerably more vigorous on this fraction, as evidenced by temperature measurements. No metal balances are available, however, to confirm this explanation.

TABLE 8. LOSS OF SULPHUR FROM SHALE ON RETORTING IN AN EXTERNALLY HEATED ROTARY FURNACE

Shale: G-1090-2 (-10 M)

Retort Temp., °F.	Retort Time, Hours	Weight Loss, Per Cent	Total S, Per Cent	Organic S, Per Cent	Sulphate S, Per Cent	Pyrite S, Per Cent	Pyrite Decomposed, Per Cent
Raw shale	-	-	6.3	0.65	0.6	5.05	-
840	14	10.2	5.19	-	-	2.55	54.0
800	24	9.0	5.44	-	-	2.81	49.6

TABLE 9. EFFECT OF SCREEN SIZE ON CHLORINATION ROASTING

Shale Used: No. 1207-100 (0.0075 per cent uranium - average of "as ground" heads).

Roasting Procedure: 40 grams of raw shale roasted in tube furnace in presence of excess chlorine for three hours at 750°F.

Leaching Procedure: Leached two hours at 180-200°F. in 200 ml. 15 per cent Na_2CO_3 solution.

Sieve Size of Shale	Per Cent of Uranium in Head	Uranium Extraction, Per Cent		
		First Series	Second Series	Average
+100	0.0071	67	67	67
-100 +200	0.0073	70	77	74
-200 +325	0.0079	80	80	80
-325	0.0079	57	53	55
"As ground"	0.0075	80	-	80

Sulphating Treatment of Shales

Sulphuric Acid Baking. A few additional experiments were run on low temperature (350°F.) baking of shale with sulphuric acid. The results indicated that retorting the ore before baking with the acid resulted in lower extractions. Acid baking improved the extraction with dilute sulphuric acid on retorted shale, as shown below:

	Raw Shale Baked 3 Hours	Retorted Shale Baked 3 Hours	Retorted Shale Not Baked
Uranium Extraction, Per Cent	70	40	5

Results do not show any advantage in sulphuric acid baking over roasting under controlled conditions in the absence of sulphuric acid.

Sulphur Trioxide Roasting. To investigate the plausibility of a sulphating mechanism in the roasting of shales, tests were run with sulphuric acid vapors as the roasting atmosphere. The following results were obtained by leaching with dilute sulphuric acid.

<u>Temperature</u>		<u>Uranium Extraction, Per Cent</u>
<u>°F.</u>	<u>°C.</u>	
930	500	70
1110	600	48
1290	700	56

These results offer some support for the sulphating-mechanism theory in that the extraction did not drop off sharply at the highest roasting temperature.

Thermal Decomposition of Uranyl Sulphate

It is believed that part of the uranium in the shales may be made available for extraction by a sulphating mechanism during the roasting process (using the sulphur present in the shales). If this is the case, thermal decomposition of the sulphate of uranium formed would be a factor in establishing the maximum recovery of the uranium. Due to the oxidizing conditions prevailing during the roasting operation, it is likely that the salt of interest is uranyl sulphate.

Samples of uranyl sulphate were heated in small diameter Pyrex glass test tubes partially immersed in a molten lead bath for various times at selected temperatures. Conditions were such as to minimize air dilution of the self-generated atmosphere in contact with the hot salt. The products were analyzed for UO_2 and UO_3 to determine the extent of thermal decomposition.

No significant difference was indicated for the various heating periods (10 minutes to 60 minutes). The essential results are:

<u>Temperature</u>		<u>UO_2,</u>	<u>UO_3,</u>
<u>°F.</u>	<u>°C.</u>	<u>Per Cent</u>	<u>Per Cent</u>
930	500	Nil	Nil
1110	600	Nil	Nil
1300	700	3	3

These data indicate that a temperature of about 1200°F. (650°C.) is safe for these conditions.

Assuming decomposition of uranyl sulphate to give SO_3 , the presence of this gas in excess of the decomposition pressure for uranyl sulphate should inhibit or reverse the thermal decomposition. As a rough check on this, a sample of uranyl sulphate was heated to about 1300°F. (700°C.) for 10 minutes in the presence of air. Some change in color was noted at this temperature. However, heating to 1400°F. (750°C.) for an additional 10 minutes appeared to convert most of the salt to a black material. Passage of sulphuric acid vapors for 10 minutes over the products in the hot furnace appeared to give almost complete reversion to the sulphate. The cooled product contained a small amount of black material insoluble in 2 per cent sulphuric acid. This indicated that the presence of sulphur trioxide may be beneficial in the roaster gases.

Leaching Studies

Leaching studies have been continued on both raw and roasted shales with the principal emphasis on utilization of the high sulphur content as a means of producing aqueous sulphuric or sulphurous acid. Although a roasting operation is required to obtain oxides of sulphur for acid production, it is necessary to compare uranium extraction on raw and roasted shale in order to determine whether the roasting step should precede or follow the leaching operation.

Leaching of Raw Shale with Dilute Acids

Dilute acids had proved so effective in extracting the solubilized uranium from roasted shales that it appeared advisable also to re-investigate their action on raw shales. Earlier work along this line had not evidenced much promise, but it was felt that, due to the marked impermeability of the raw shales, a considerable improvement could be expected with more finely divided material. The results of the tests are shown in Table 10.

The initial series of acid leaches of raw ore indicated that there was very little difference between equal concentrations of sulphuric, nitric, or hydrochloric acids, in either extraction or in total solids dissolved. Consequently, only sulphuric acid was used for the subsequent tests, since this acid will presumably be readily available as a by product of the process.

Forty to forty-five per cent of the contained uranium was readily extracted in dilute acid leaches at room temperature. Moderate variations in time, concentration, or particle size appeared to affect the results very little.

Increasing the temperature gave a significantly higher extraction, but the total solids dissolved also increased. Raising the acid concentration of a hot leach from 2 to 4 per cent increased the extraction from 64 to 77 per cent. No quantitative data are available on other interfering elements in the solutions, but they are believed to be relatively high, particularly in the case of iron and aluminum.

TABLE 10. LEACHING OF RAW SHALE WITH DILUTE ACIDS

Shale Used: No. 1207-100 (0.0075 per cent uranium) "as ground" and screened -325M fraction.

Leaching Procedure: 50-gram samples of raw shale were leached in 200 ml. of acid of strength (wt. per cent) shown.

Size of Shale	Acid	Per Cent of Soln.	Per Cent Based on Ore	Time, Hours	Temperature, °F.	Loss in Weight, Per Cent	Uranium Extracted, Per Cent
As ground	H ₂ SO ₄	2.0	8.0	4	R.T.	-	43 (1)
Ditto	HNO ₃	2.0	8.0	4	Ditto	1.6	45 (1)
"	HCl	2.0	8.0	4	"	1.6	40 (1)
"	H ₂ SO ₄	2.0	8.0	2	"	1.0	45
"	Ditto	2.0	8.0	4	"	1.2	43
-325M	"	2.0	8.0	2	"	2.2	45
-325M	"	2.0	8.0	4	"	1.3	43
As ground	"	4.0	16.0	2	"	1.0	45
As ground	"	4.0	16.0	4	"	1.8	51 (2)
-325M	"	2.0	8.0	1	180	3.4	64 (2)
-325M	"	4.0	16.0	1	180	3.2	69 (2)
As ground	"	2.0	8.0	2	180	2.8	64
As ground	"	4.0	16.0	2	180	3.4	77
-325 M	"	2.0	8.0	2	180	3.6	64
-325M	"	4.0	16.0	2	180	4.0	77

See next page for footnotes.

TABLE 10. (CONTINUED)

Footnotes

- (1) Residues from these acid leaches were roasted 3.5 hours at 1020°F. and re-leached two hours at R.T. in 2 per cent H_2SO_4 producing an additional 35-37 per cent extraction. Total extractions ranged from 75-80 per cent.
- (2) Residues were roasted six hours at 1020°F. and re-leached three hours at 180°F. in 2 per cent H_2SO_4 , producing an additional 18-21 per cent extraction. Total extractions were 85-87 per cent.

It was thought that there was some possibility that the uranium which was acid soluble in the raw state might be the portion that was nonsoluble after roasting. Present data do not substantiate this hypothesis, but it was noted that additional uranium could be extracted by roasting and re-leaching the acid leach residues. In one series, in which both leaches were at room temperature, additional extractions of 35-37 per cent were secured, producing a total of 75-80 per cent. In another, in which both leaches were at 180-200°F. (80-95°C.), the additional extraction was only 18-21 per cent, but with the higher initial extraction produced totals in the 85-87 per cent range.

Additional data on the amounts of iron and aluminum dissolved by sulphuric acid from raw and roasted shale are needed before a decision can be made on the best type of feed for the leaching operation.

Leaching of Roasted Shale at Room Temperature

Leaching at room temperature would be a more practical procedure on a plant scale than leaching at elevated temperatures. An investigation of room-temperature leaching has demonstrated its feasibility, at least for dilute acid media. Dilute sodium carbonate solutions were quite ineffective in extracting the uranium; relatively strong (15 per cent) ammonium carbonate solutions were not much more effective.

The data are shown in Table 11 and it is apparent that either dilute sulphuric or nitric acid readily extracted the solubilized uranium.

TABLE 11. LEACHING OF ROASTED SHALE AT ROOM TEMPERATURE

Shale Used: G-1207-100 (0.0075 per cent U) "as ground".

Preliminary Treatment: 4-, 12-, 24-, and 72-hour samples were muffle roasted 4-8 hours at 840-1020°F.
1- and 2-hour samples were roasted 16 hours at 1020°F. in tube furnace.

Leaching Procedure: 50-gram (equivalent) samples were agitated in 200 grams of solution of strength (weight per cent) shown. Control leach in 15 per cent Na_2CO_3 at 180-200°F. for 3 hours.

Leach Solution	Uranium Extracted, Per Cent					
	Leaching Time, Hours					
	1	2	4	12	24	72
15% Na_2CO_3	72(1)	-	-	67(1)	64(1)	59(1)
2% Na_2CO_3	-	-	37	43	45	43
15% $(\text{NH}_4)_2\text{CO}_3$	-	-	56	56	53	53
2% H_2SO_4	72(2)	72(2)	67	64	64	64
1.4% HNO_3	72(2)	72(2)	67	64	67	59

(1) Control leach - 3 hours at 180-200°F. in 15 per cent Na_2CO_3 .

(2) One- and two-hour leaches performed on a different roast batch which gave higher extraction.

The data also indicate that extraction was quite rapid, proceeding in as short a time as one hour in the laboratory tests.

Loss in weight on leaching ranged from 3.5-4.5 per cent for the dilute acid leaches, which is substantially lower than produced by strong acid leaches. Analytical data indicate that dissolution of contaminating ions increases with increasing time of contact. Some reduction of these interfering ions may be possible by employing only minimum leaching times, since it appears that only a brief contact time is needed to dissolve most of the uranium.

In another test, a sample of roasted No. 1207-108 shale was leached in 300 ml. of 1.8 per cent sulphuric acid for approximately one hour at room temperature. The shale had been roasted in the larger scale rotary furnace for four hours at 1110°F. (600°C.), and was incompletely roasted. The extraction secured was only 26 per cent.

A similar test on another larger scale roast (14 hours) resulted in only 36 per cent extraction, even though leaching time was increased to two hours. The conclusions are that the short roasting time did not permit full solubilization of the uranium; and that this is prerequisite to satisfactory extraction with dilute mineral acids at room temperature.

Uranium Enrichment of Sulphuric Acid Leach Solutions

Practical recovery of uranium from leach solutions obviously will require richer solutions than those attained in the usual laboratory tests. A preliminary investigation was conducted to determine the feasibility of increasing uranium concentration in leach solutions, and to determine the amounts of undesired contaminants also accruing.

Four 200-gram samples of 1207-100 shale were roasted 11-14 hours at 930-1020°F. (500-550°C.) in a tube furnace. These roasted samples were leached successively with 150 ml. of 2 per cent sulphuric acid solution. Each filter cake was washed with only enough water to maintain the 150 ml. volume. Before each leach, 3 grams of sulphuric acid was added to the filtrate from the preceding leach in order to maintain a low pH.

Solution I contained 22.3 mg. of uranium, which represents approximately 150 mg. per liter and accounts for about 37 per cent of the uranium in the head. Solution II contained 17 mg. of uranium, a concentration of 110 mg. per liter, and accounted for 28 per cent of the uranium. The total recovery was therefore in the range of 65 per cent, even with admittedly incomplete washing.

It is believed that a concentration of 150 mg. per liter would be practical for the recovery of uranium from solution, and there is reason to believe that this concentration can be further increased.

Data on contaminating ions are as yet incomplete but preliminary results indicate that iron and aluminum are present in Solution II in a ratio of 100-120 times the uranium.

In another series of successive leaches, in which no make-up acid was added, very little uranium was found in the final solution. In this series, the pH had risen to about 3.1, which was apparently too high to keep uranium in solution.

A ten-stage series of countercurrent leaching tests is underway to determine the effect of contaminant buildups on uranium extraction from roasted ore. Two per cent sulphuric acid is the lixiviant and a pulp density of 50 per cent is being employed. Only preliminary data are at present available, but they indicate that 65-70 per cent extraction was attained and that the maximum concentration of uranium was about 100 mg. per liter.

Leaching with Aqueous Solutions of "Off-Gases"

There appear to be definite advantages in using the roaster gases (containing the oxides of sulphur evolved from the shale) directly to prepare an aqueous solution for use as a lixiviant. This would eliminate the need for conversion to sulphuric acid and would simplify the process. The original exploratory test in which a saturated aqueous solution of off-gases was used as the lixiviant also revealed a considerable decrease in the pickup of other contaminants such as iron and aluminum as indicated in Table 12.

From the standpoint of the recovery of uranium from leach solutions, the suppression of iron and aluminum was of definite interest and further tests were made to confirm the preliminary results. It was soon learned that the desired suppression of interfering elements required the establishment of certain conditions, all of which are not yet known. The only procedure yet found to produce the desired results necessitated heating the off-gas solution prior to leaching, and the use of a hot leach.

TABLE 12. COMPARISON OF "OFF-GAS" LEACH SOLUTION
AND SULPHURIC ACID LEACH SOLUTION

Leach Solution	Composition of Solution after Leaching, mg./Liter				
	U	Fe	Al	SO ₄ ⁼	SO ₃ ⁼
Water saturated with off-gases	4.6	26	10	144	16
1 per cent sulphuric acid	4.8	300	340	-	-

One test in which this procedure was followed showed 21 mg./liter of Fe and 68 mg./liter of Al for a comparable extraction of uranium.

Analysis of a sample of off-gas solution indicated 0.49 gram of SO_3^- /liter and 0.55 gram of SO_4^- /liter. Heating such a solution prior to use probably decreased the SO_3^- to a negligible value, so that the final solution is, in all probability, a weak sulphuric acid solution.

Further work is planned to fix the important variables in off-gas leaching more precisely and to demonstrate whether or not it is a sufficiently effective lixiviant.

Leaching with Aqueous Solutions of Sulphur Dioxide

As an outgrowth of the work on leaching with aqueous solutions of off-gases, sulphurous acid was investigated as a lixiviant. The results presented in Table 13 show a maximum uranium extraction of 59 per cent on roasted shale under the conditions used, which compared with 67 per cent for a control leach using hot 15 per cent sodium carbonate solution. Leaching with aqueous solutions of sulphur dioxide was more successful on roasted shale than on raw shale.

The results on roasted shale are somewhat encouraging and indicate the need for further investigation of the variables in sulphurous acid leaching. The effects of particle size, sulphur dioxide concentration, leaching time, and temperature need to be studied in greater detail, and information is needed on the amounts of interfering ions carried into the leach solutions.

TABLE 13. LEACHING OF SHALE WITH AQUEOUS SOLUTIONS OF SULPHUR DIOXIDE

Shale Used: G-1207-100 (0.0075 per cent U) "as ground" (27.5 per cent, +100 mesh; 43 per cent, -325 mesh) and -325 mesh.

Leaching Procedure: 50 grams of raw shale or roasted equivalent was suspended in 200 cc. of H_2O saturated with SO_2 ; additional SO_2 was slowly bubbled through during leaching at room temperature (80-85°F.).

Shale	Size	Time, Hours	Uranium Extraction, Per Cent
Raw	"As ground"	2	35
Raw	"As ground"	4	25
Raw	-325 mesh	2	32
Raw	-325 mesh	4	26
Roasted	"As ground"	2	48
Roasted	"As ground"	4	59
Roasted	"As ground"	8	53

Comparison of Carbonate Leaching on Different Roasted Shales

A comparative roasting and leaching investigation was conducted on nine different lots of shale, ranging in uranium analysis from 0.0055 per cent to 0.0098 per cent. Twenty-seven determinations were made; two samples of each shale being muffle roasted, and one being tube roasted. All samples were leached in 15 per cent sodium carbonate solutions at 180-200°F.

The results are recorded in Table 14 and indicate that over the range studied differences in behavior are relatively minor. It is difficult to discern any increase in extraction with increasing uranium content of the shale.

The results reveal that an oxidizing roast followed by a carbonate leach can be expected to extract approximately 55 per cent of the uranium, with an average concentration of 0.0037 per cent being left in the residue. The use of a dilute sulphuric acid leach might be expected to increase slightly the per cent extraction but probably to not over 65-70 per cent. These studies show that the procedure used in this series of tests can be applied to a wide variety of shales with reasonably good results. With the exception of Shale No. 1207-101A, all of the samples gave uranium extractions of about 55 to 65 per cent.

Miscellaneous Leaching Studies

Several experiments were conducted in which successive leaches were carried out with different reagents on the same batch of roasted shale. Most of this work was done with dilute sulphuric acid and 15 per cent sodium carbonate solution. In general, there was no significant increase in

TABLE 14. SUMMARY DATA - COMPARATIVE CARBONATE LEACHES OF VARIOUS SHALES

Roasting Conditions: Muffle roasts at 930°F. for 6 hours; tube roast at 1020°F. for 4 hours.

Leaching Conditions: 15 per cent sodium carbonate solution at 180°F. for 4 hours.

		B. M. I. Shale Number									
		1207- 103A	1090- 4	1207- 101A	1207- 103B	1090- 1	1207- 100	1207- 101C	1207- 102	1207- 105	
Reported % U in head		0.0055	0.0060	0.0064 ⁽¹⁾	0.0065	0.0070	0.0075	0.0075	0.0080	0.0098 ⁽²⁾	
mg. U in 50 g. sample		2.75	3.00	3.20	3.25	3.50	3.75	3.75	4.00	4.90	
<u>Muffle Roast I</u>											
mg. U in soln.		1.3	1.4	1.2	1.4	2.0	2.1	2.1	2.4	2.9	
mg. U in residue		1.6	1.2	1.8	1.5	1.6	1.6	1.6	1.5	1.9	
mg. U total		2.9	2.6	3.0	2.9	3.6	3.7	3.7	3.9	4.8	
% U found		105	87	92	91	103	99	99	98	97	
% extraction		47	47	37	44	57	56	56	60	59	
% U in residue		0.0041	0.0032	0.0045	0.0040	0.0042	0.0042	0.0040	0.0038	0.0048	
<u>Muffle Roast II</u>											
mg. U in soln.		1.6	1.7	1.5	1.7	1.8	2.6	2.2	2.4	2.9	
mg. U in residue		1.2	1.1	1.4	1.1	1.2	1.4	1.4	1.2	1.5	
mg. U total		2.8	2.8	2.9	2.8	3.0	4.0	3.6	3.6	4.4	
% U found		106	93	89	88	86	107	96	88	90	
% extraction		58	57	46	53	51	69	59	60	59	
% U in residue		0.0031	0.0028	0.0036	0.0029	0.0031	0.0036	0.0035	0.0031	0.0038	
<u>Tube Roast I</u>											
mg. U in soln.		1.7	2.0	1.5	2.0	1.9	2.6	2.3	2.4	2.9	
mg. U in residue		1.6	1.0	1.8	1.2	1.5	1.5	1.5	1.3	1.6	
mg. U total		3.3	3.0	3.3	3.2	3.4	4.1	3.8	3.7	4.5	
% U found		120	100	101	100	97	112	101	93	92	
% extraction		62	67	46	63	54	69	61	60	59	
% U in residue		0.0042	0.0026	0.0047	0.0033	0.0039	0.0039	0.0038	0.0034	0.0041	

TABLE 14. (CONTINUED)

		B. M. I. Shale Number									
		1207-103A	1090-4	1207-101A	1207-103B	1090-1	1207-100	1207-101C	1207-102	1207-105	
<u>Averages</u>											
Average % U found		109	93	96	94	94	104	99	93	94	
Average % extraction		56	57.	43	53	54	65	59	60	59	
Average % U in residue		0.0038	0.0029	0.0042	0.0034	0.0037	0.0039	0.0038	0.0034	0.0042	
Over-all Average, % U Found = 98 Per Cent											
Over-all Average, % Extraction = 56.5 Per Cent											
Over-all Average, % U in Residue = 0.0037 Per Cent											

(1) This was a grab sample from an 85-pound lot of Shale No. 1207-101A, which contains on the average 0.0070 per cent uranium.

(2) Grab sample from 200-pound lot of No. 1207-105, which contains on the average 0.0080 per cent uranium.

extraction of uranium with different reagents over what was obtained by successive leaching with the same reagent.

In another set of experiments, oxalic acid was found to be no more effective than sulphuric acid as a lixiviant for roasted shale.

There were some indications that addition of potassium chlorate or hydrofluoric acid to dilute sulphuric acid increased the extraction of uranium from shale, but neither addition gave extraordinary results.

PLANS FOR FUTURE WORK

Considerable attention will be given to developing roasting techniques on a larger scale with particular emphasis on fluidization studies.

Leaching studies will be concerned mainly with utilization of sulphuric or sulphurous acid, both of which can be produced from the sulphur in the shale. Countercurrent leaching studies with sulphuric acid are underway to provide information on the amounts of uranium, iron, aluminum, and other materials dissolved from roasted shale.

Future work will also involve a study of methods of recovering the uranium from leach solutions. This phase of the work has been delayed pending the selection of a suitable solution for leaching. Although subsequent leaching studies may alter the situation, it now appears that dilute sulphuric acid is the most probable selection.